

Acta Cryst. (1956). 9, 1019

Crystallographic Studies of Perovskite-like Compounds. II. Rare Earth Aluminates*

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(Received 13 April 1956 and in revised form 29 May 1956)

The aluminates of the trivalent ions of Gd, Eu, and Sm are isostructural with GdFeO_3 . They belong to space group $D_{2h}^{16}-Pbnm$ with four distorted perovskite units in the true crystallographic cell. The aluminates of the trivalent ions of Nd, Pr and La are rhombohedral belonging to space group $D_{3d}^5-R\bar{3}m$ with two formula units in the unit cell. These crystals bear a very close structural relationship to the orthorhombic ones.

LaAlO_3 undergoes a transition at $435 \pm 25^\circ \text{C.}$ to the simple cubic cell containing one formula unit. Evidently, the transition is one of higher than first order. There is no crystallographic transition of PrAlO_3 below 950°C. but a gradual change toward the cubic phase similar to that in LaAlO_3 is indicated.

Introduction

The investigation described in this paper is a continuation of the work on crystallographic studies of perovskite-like structures begun recently when Remieka (1956) of our Laboratories evolved a method for growing crystals (of size suitable for X-ray and optical examination) of such compounds. The availability of these crystals has enabled us to elucidate the structural features of a large number of these compounds. The crystal structure of gadolinium orthoferrite, GdFeO_3 , has been worked out in some detail (Geller, 1956) and crystallographic studies of several other rare earth orthoferrites, as well as YFeO_3 , YCrO_3 and YAlO_3 , were reported in the first paper of this series (Geller & Wood, 1956), hereinafter referred to as I.

The aluminates form a particularly interesting series within which at room temperature there exist compounds belonging to at least two different structural types. The aluminates of the trivalent ions of Gd, Sm and Eu are isostructural with GdFeO_3 , which belongs to space group $D_{2h}^{16}-Pbnm$ with four distorted perovskite units in the true crystallographic cell, whereas the aluminates of the trivalent ions of Nd, Pr and La belong to space group $D_{3d}^5-R\bar{3}m$ with two formula units per unit cell. This new structure is closely related to the previous one.

Crystallographic data on the aluminates

Powder photographs were taken of all the compounds with Cr K radiation. By comparison with the diffraction data from the orthoferrites as well as those from YAlO_3 the powder photographs of the aluminates of Gd, Sm and Eu were indexed on the orthorhombic cell

(see Tables 1 and 2). The powder photographs of the aluminates of Nd, Pr, and La indicated that these compounds were closely related in structure to the other aluminates (see Tables 1, 2 and 3). However, it was also early apparent that they were of a different type. For example, the equivalent of the $\{111\}$ orthorhombic reflections was not present. (This could not be a result of anomalous scattering of the Cr $K\alpha$ by the L electrons of the particular rare earth ions). This was also the case with such reflections as $\{023\}$, $\{221\}$, $\{115\}$, $\{225\}$, and $\{421\}$.*

Optical examination by E. A. Wood of some of the single crystals of PrAlO_3 established that these crystals are rhombohedral. Subsequent optical examination of the NdAlO_3 and LaAlO_3 crystals indicated that these crystals are also rhombohedral. All of the sizeable crystals examined optically appeared to be twinned.

A single crystal of PrAlO_3 was mounted on a goniometer head and aligned accurately along a rational direction by means of the Hendershot (1937) method. A heavily exposed oscillation photograph (Mo K radiation) of this crystal indicated an identity period of 7.5 \AA , but one had to examine this photograph very closely to find the few very weak reflections in the odd layers. These could easily have been missed were it not for the realization that the structure of this compound was known to be closely related to the orthorhombic structure. The oscillation photograph also indicated an apparent plane of diffraction symmetry perpendicular to the oscillation axis: this was also somewhat misleading.

Buerger precession photographs (Mo K radiation) indicated a high symmetry, possibly tetragonal or

* This name is used for convenience and should not imply the existence of discrete aluminate ions.

* The transformation of these indices to the B -centered monoclinic cell results in mixed indices, which reflections therefore do not exist in the face-centered rhombohedral case; see below.

Table 1. Powder diffraction data for the

Orthorhombic indices	GdAlO ₃			EuAlO ₃			SmAlO ₃			C.Rh.
	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>	
110	3.712	{ 3.730	<i>m-s</i>	3.717	{ 3.734	<i>m-s</i>	3.725	{ 3.739	<i>m-s</i>	020
002		{ 3.723			{ 3.730			{ 3.737		
111	3.321	{ 3.336	<i>w</i>	3.325	{ 3.339	<i>w</i>	3.324	{ 3.343	<i>vw</i>	
020	2.646	{ 2.648	<i>vw</i>		{ 2.646			{ 2.645		022
112		{ 2.638		2.632	{ 2.639	<i>vs</i>	2.636	{ 2.643	<i>vs</i>	220
200	2.629	{ 2.623	<i>vs</i>		{ 2.636			{ 2.642		
021	2.491	{ 2.498	<i>w</i>	2.489	{ 2.494	<i>w</i>	2.498	{ 2.493	<i>vw</i>	
103		{ 2.244		2.245	{ 2.249	<i>vw</i>	2.250	{ 2.253	<i>vw</i>	131
211	2.241	{ 2.243	<i>vw</i>		{ 2.249			{ 2.254		131
022	2.158	{ 2.160	<i>m</i>		{ 2.158			{ 2.159		222
202	2.142	{ 2.145	<i>m</i>	2.151	{ 2.152	<i>m-s</i>	2.155	{ 2.158	<i>m-s</i>	222
113	2.063	{ 2.067	<i>vw</i>	2.066	{ 2.070	<i>vw</i>				
220		{ 1.865		1.862	{ 1.867	<i>m-s</i>	1.867	{ 1.869	<i>m-s</i>	040
004	1.861	{ 1.862	<i>m-s</i>		{ 1.865			{ 1.868		
023		{ 1.812		1.810	{ 1.812	<i>w-m</i>	1.811	{ 1.813	<i>w</i>	
221	1.808	{ 1.809	<i>w-m</i>		{ 1.811			{ 1.814		
213		{ 1.707		1.712	{ 1.711	<i>vw</i>				331
301	1.707	{ 1.703	<i>vw</i>		{ 1.710					331
114		{ 1.666		1.668	{ 1.668	<i>m-s</i>	1.672	{ 1.671	<i>m-s</i>	042
310	1.665	{ 1.661	<i>m-s</i>		{ 1.668			{ 1.671		240
131	1.633	{ 1.635	<i>w-m</i>	1.631	{ 1.632	<i>m</i>	1.631	{ 1.632	<i>w</i>	
132		{ 1.528			{ 1.526			{ 1.527		224
024	1.525	{ 1.524	<i>m</i>	1.522	{ 1.524	<i>vs</i>	1.525	{ 1.526	<i>vs</i>	242
204		{ 1.518			{ 1.522			{ 1.526		242
312	1.517	{ 1.517	<i>s</i>		{ 1.522					
223	1.490	{ 1.491	<i>vw</i>	1.492	{ 1.493	<i>vw</i>	1.494	{ 1.495	<i>vw</i>	
133		{ 1.389			{ 1.388			{ 1.389		
115	1.387	{ 1.383	<i>w-m</i>	1.387	{ 1.385	<i>w-m</i>	1.388	{ 1.388	<i>w-m</i>	
313					{ 1.385			{ 1.388		
040	1.325	{ 1.326	<i>vw-w</i>	1.323	{ 1.323	<i>vw</i>		{ 1.323		044
224		{ 1.318		1.319	{ 1.319	<i>s</i>	1.321	{ 1.321	<i>m-s</i>	
400	1.317	{ 1.312	<i>s</i>		{ 1.318			{ 1.321		440
041	1.304	{ 1.305	<i>vw-w</i>	1.303	{ 1.303	<i>vw-w</i>	1.301	{ 1.302	<i>w</i>	
025					{ 1.300			{ 1.301		
140	1.284	{ 1.283	<i>vw</i>	1.283	{ 1.283	<i>vw</i>	1.283	{ 1.283	<i>vw</i>	
233	1.263	{ 1.262	<i>vw</i>	1.260	{ 1.263	<i>vw-w</i>	1.264	{ 1.264	<i>vw</i>	
411	1.258	{ 1.255	<i>vw</i>		{ 1.260			{ 1.263		
042		{ 1.249		1.245	{ 1.247	<i>vw</i>		{ 1.247		244
134	1.245	{ 1.245	<i>vw</i>		{ 1.245			{ 1.246		060
006		{ 1.241			{ 1.243		1.246	{ 1.246	<i>m-s</i>	442
314		{ 1.239		1.243	{ 1.243	<i>m-s</i>		{ 1.246		442
402	1.239	{ 1.237	<i>m</i>		{ 1.243			{ 1.246		
331	1.226	{ 1.226	<i>w-m</i>	1.228	{ 1.228	<i>w-m</i>	1.230	{ 1.229	<i>w</i>	
240	1.184	{ 1.183	<i>vw</i>	1.183	{ 1.182	<i>vw-w</i>		{ 1.183		062
332	1.180	{ 1.179	<i>w</i>	1.181	{ 1.181	<i>w-m</i>	1.183	{ 1.182	<i>s</i>	
116		{ 1.178		1.179	{ 1.180	<i>s-vs</i>		{ 1.182		260
420	1.178	{ 1.178	<i>s-vs</i>		{ 1.180			{ 1.182		
241	1.169	{ 1.169	<i>m</i>	1.168	{ 1.168	<i>m-s</i>		{ 1.168		
225	1.164	{ 1.164	<i>w-m</i>	1.166	{ 1.166	<i>m</i>	1.168	{ 1.167	<i>m</i>	
421	1.162	{ 1.161	<i>vw-w</i>		{ 1.165			{ 1.168		

1. *s* = strong, *m* = medium, *w* = weak, *v* = very.2. ov. (*hkl*) = This line overlaps the (*hkl*) line.

3. Indices given for the aluminates:

F.C.Rh. = face-centered rhombohedral;

Rh. = primitive rhombohedral;

Hex. = triply primitive hexagonal.

cubic, and also that the 7.5 Å identity period was correct; but again the latter was based on a very few weak reflections. The Weissenberg photographs were more illuminating. These could be interpreted on the basis of twinning on the (100) plane of an apparently 'nearly cubic' face-centered rhombohedral cell with 7.5 Å edge. All of the even layers gave many intense reflections, whereas the first layer with over four times

the exposure (90 hr., Mo *K* radiation, 45 kVp., 20 mA.) of any of the even layers gave very few reflections, most of them weak.

It was shown that in GdFeO₃ (Geller, 1956) the direction of the pseudocell axes are along the [110], [110] and [001] directions of the orthorhombic cell. It was also pointed out that in most of the crystals of the nine compounds discussed in I, the major faces

data for the rare earth aluminates (Cr $K\alpha$ radiation)

Indices				NdAlO ₃			PrAlO ₃			LaAlO ₃		
<i>I</i>	C.Rh.	Rh.	Hex.	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>	<i>d</i> _o (Å)	<i>d</i> _c (Å)	<i>I</i>
<i>m-s</i>	020	110	01.2	3.743	3.749	<i>s</i>	3.750	3.762	<i>s</i>	3.797	3.791	<i>s</i>
<i>vw</i>	02 $\bar{2}$	10 $\bar{1}$	11.0	2.650	{ 2.660	<i>vs</i>	2.656	{ 2.667	<i>vs</i>	2.657	{ 2.683	<i>vs</i>
<i>vs</i>	220	211	10.4		2.643			2.654			2.678	
<i>vw</i>	1 $\bar{3}$ 1	11 $\bar{1}$	02.1	2.263	{ 2.267	<i>vw-w</i>	2.267	{ 2.274	<i>vw-w</i>	2.286	{ 2.288	<i>vw-w</i>
<i>vw</i>	13 $\bar{1}$	210	11.3		2.262			2.270			2.286	
<i>m-s</i>	22 $\bar{2}$	200	20.2	2.168	2.169	<i>s</i>	2.173	2.176	<i>s</i>	2.188	2.190	<i>s</i>
	222	222	00.6	2.149	2.151	<i>w-m</i>	2.159	2.159	<i>w-m</i>		2.185	
<i>m-s</i>	040	220	02.4	1.874	1.875	<i>s</i>	1.879	1.871	<i>s</i>	1.896	1.895	<i>s</i>
<i>w</i>												
<i>m-s</i>	3 $\bar{3}$ 1	20 $\bar{1}$	21.1	1.722	{ 1.725	<i>vw</i>	1.728	{ 1.730	<i>vw</i>	1.736	{ 1.741	<i>vw</i>
	33 $\bar{1}$	311	20.5		1.719			1.725			1.739	
	04 $\bar{2}$	21 $\bar{1}$	12.2	1.681	1.681	<i>w-m</i>	1.687	1.686	<i>w-m</i>	1.696	1.696	<i>m</i>
	240	321	11.6	1.671	1.672	<i>w-m</i>	1.679	1.679	<i>w-m</i>		1.694	
<i>w</i>	22 $\bar{4}$	21 $\bar{1}$	30.0	1.532	{ 1.536	<i>s</i>	1.536	{ 1.540	<i>s</i>	1.548	{ 1.549	<i>s</i>
<i>vs</i>	24 $\bar{2}$	310	21.4		1.532			1.537			1.548	
	242	332	01.8	1.521	1.523	<i>w</i>	1.528	1.530	<i>w-m</i>		1.545	
<i>vw</i>												
<i>w-m</i>												
<i>m-s</i>	04 $\bar{4}$	20 $\bar{2}$	22.0	1.329	1.330	<i>w-m</i>	1.332	1.333	<i>w-m</i>	1.342	1.341	<i>w-m</i>
	440	422	20.8	1.321	1.322	<i>m</i>	1.326	1.327	<i>m</i>	1.339	1.339	<i>m</i>
<i>w</i>												
<i>vw</i>												
<i>vw</i>												
<i>m-s</i>	24 $\bar{4}$	30 $\bar{1}$	31.2	1.253	1.253	<i>vw-w</i>	1.257	1.257	<i>vw-w</i>	1.264	{ 1.264	<i>m</i>
	060	330	03.6	1.250	1.250		<i>w-m</i>	1.254				
	44 $\bar{2}$	411	30.6	1.243	1.243	<i>vw-w</i>		1.249	1.249			
	442	433	10.10									
<i>v</i>	06 $\bar{2}$	32 $\bar{1}$	13.4	1.188	1.188	<i>m</i>	1.192	1.192	<i>m</i>	1.199	1.199	<i>m</i>
	260	431	12.8	1.184	1.183	<i>m-s</i>	1.188	1.188	<i>m-s</i>	1.198	1.198	<i>m-s</i>
<i>n</i>												

4. To facilitate the arrangement of this table, reflections from the rhombohedral crystals are arranged so that they lie near those of the orthorhombic to which they are related. In most cases, one orthorhombic form will contribute members to more than one face-centered rhombohedral form. Also, for the sake of brevity, reflections not observed in YAlO₃ (see Table 1 of I) were omitted even when they overlapped others as, for example, the orthorhombic (222) are 1.668, 1.670, 1.672 respectively.

developed are (110) and (001). Thus in those crystals the crystal habit is influenced very strongly by the pseudocell rather than by the true crystallographic cell. This is also the case with PrAlO₃.

One may picture the situation as follows (see Fig. 1): Consider the *B*-centered monoclinic cell formed from the orthorhombic cell of the GdFeO₃-type structure which is most often the growth cell of compounds

belonging to this type. The growth rhomb of PrAlO₃ is closely related to this *B*-centered monoclinic cell, i.e. the faces of the perovskite-like pseudocells as formed by the Al³⁺ ions at corners are parallel to the faces of the growth rhomb. As in the case of the *B*-centered monoclinic cell, which contains eight formula units, the growth rhomb of PrAlO₃ also contains eight formula units, and because this cell is face-

Table 2. *Crystallographic data on the orthorhombic aluminates*

Com- pound	Lattice constants			Vol. per unit cell (Å ³)	X-ray density (g.cm. ⁻³)	Pseudocell dimensions		
	a (Å)	b (Å)	c (Å)			a (= c) (Å)	b (Å)	β (°)
GdAlO ₃	5.247	5.304	7.447	207.3	7.43	3.731	3.724	90.6
EuAlO ₃	5.271	5.292	7.458	208.0	7.25	3.734	3.729	90.2
SmAlO ₃	5.285	5.290	7.473	208.9	7.16	3.739	3.737	90.1
YAlO ₃	5.179	5.329	7.370	203.4	5.35	3.716	3.685	91.6

Table 3. *Crystallographic data on the rhombohedral aluminates*

Com- pound	Simplest cell		Triply primitive hexagonal cell		Vol. per simplest unit cell (Å ³)	X-ray density (g.cm. ⁻³)	Pseudocell dimensions*	
	a (Å)	α	a (Å)	c (Å)			a (Å)	α
NdAlO ₃	5.286	60° 25'	5.319	12.91	105.4	6.91	3.750	90° 22'
PrAlO ₃	5.307	60 20	5.334	12.97	106.5	6.73	3.762	90 17
LaAlO ₃	5.357	60 6	5.365	13.11	108.9	6.52	3.790	90 5

* The face-centered rhombohedral cell has the cell edge 2a and the same angle α.

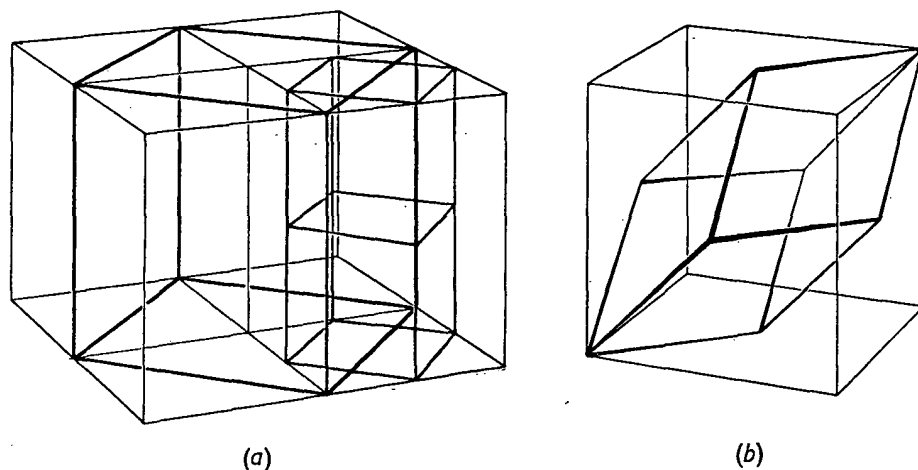


Fig. 1. (a) A sketch indicating how the *B*-centered monoclinic or face-centered rhombohedral cell is derived from the orthorhombic cell. Two of the perovskite like pseudocells are also shown.

(b) A sketch indicating how the primitive rhombohedral cell is derived from the face-centered rhombohedral cell.

centered, the primitive rhombohedral cell contains 2 formula units. Because the growth rhomb has very nearly cubic dimensions, the true cell has very nearly the dimensions of the very special rhombohedral unit cell which derives from the face-centered cubic cell, i.e. the rhombohedral angle of the primitive cell of the PrAlO₃ is very nearly 60°. The relations between the face-centered and primitive rhombohedral cells are as follows:

$$a_p = \frac{1}{2}a_f / \{2(1 + \cos \alpha_f)\}, \quad \cos \alpha_p = \frac{1}{2} \frac{3 \cos \alpha_f + 1}{\cos \alpha_f + 1};$$

or

$$a_f = a_p / \{3 - 2 \cos \alpha_p\}, \quad \cos \alpha_f = \frac{2 \cos \alpha_p - 1}{3 - 2 \cos \alpha_p};$$

where the subscripts *p* and *f* denote the primitive and face-centered cells respectively.

The powder photographs of the compounds with the rhombohedral structure were the most suitable to use for determination of lattice constants. These were rather easily indexed as follows: Lines of very close

spacing were grouped together and each group assigned to a given value of $(h^2 + k^2 + l^2)$ referred to the growth rhomb in the obvious way. The number of possibilities for each $(h^2 + k^2 + l^2)$, multiplicity and intensity were considered. It was thereby possible to assign indices to all of the lines. The growth-rhomb indices were transformed to those of the true rhomb and the latter in turn to hexagonal indices for ease of calculation. The highest-angle lines were used to calculate the hexagonal axes. The *d* spacings were then calculated using IBM equipment. The results are shown in Table 1, in which calculated *d* spacings are compared with observed. The agreement is seen to be rather good.

With regard to the structure of the rhombohedral compounds, it may be seen in Table 1 that only two very weak lines in the powder photographs indicate that the unit cell contains two formula units. If these two lines were accidentally overlooked, the photographs could be indexed on a cell of half the volume of the true cell. The single-crystal photographs, as

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well as the comparison of the powder photographs with those of the orthorhombic structure, establish that these two lines do indeed belong to the patterns of these compounds. Examination of the single-crystal photographs indicates that these compounds most probably belong to space group $D_{3d}^5-R\bar{3}m$. The Al^{3+} ions are in positions 1(a): 0, 0, 0 and 1(b): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; the A^{3+} (Nd, Pr and La) ions are in 2(c): $\pm(x, x, x)$ and the O^{2-} in 6(h): $\pm(x, x, z; \odot)$. For the following conditions the Pr^{3+} and O^{2-} ions would make no contribution to reflections with $(h+k+l)_{rh} = 2n+1$: $x_{Pr} = \frac{1}{4}$; $x_O = \frac{1}{4}$; $z_O = -\frac{1}{4}$. Under these conditions, of course, the simplest unit cell would contain only one formula unit, as mentioned above. This cell would have the orientation of the face-centered rhombohedral cell described above; it would still belong (if centrosymmetric) to space group $R\bar{3}m$ with Al^{3+} in 1(a), Pr^{3+} in 1(b) and O^{2-} in 3(d): $(\frac{1}{2}, 0, 0; \odot)$. Actually, in the true cell the parameter of the rare earth ions does not differ much from $\frac{1}{4}$ but it is not practicable to determine the oxygen parameters accurately at this time because of the twinning of all crystals of a size suitable for X-ray investigation as well as the 'swamping' of the oxygen ion scattering by that of the heavy rare earths.

Crystallographic data on the orthorhombic and rhombohedral aluminates are given in Tables 2 and 3 respectively.

High-temperature studies

Not the least interesting aspect of the study of the perovskite-like compounds is the possibility of crystallographic transitions with changing temperature. In the case of the aluminates, it appeared likely that the rhombohedral aluminates might undergo a transition to the simple cubic structure.

The most suitable choice appeared to be $LaAlO_3$ (see Table 3). A series of powder photographs was taken at temperatures ranging from 125 to 650° C. (the camera used was designed and built by W. L. Bond of these Laboratories). A gradual change from the rhombohedral to the cubic structure was noted. The resolving power of the X-ray method was not great enough to allow the accurate determination of the transition temperature. At 350° C. there was no evidence of line splitting, but this cannot be accepted as ultimate proof. E. A. Wood examined some very small apparently unstrained crystals of $LaAlO_3$ with a hot-stage microscope (Wood, 1951) and determined that the crystals become isotropic at $435 \pm 25^\circ C$.

Several of the photographs in the $LaAlO_3$ series were measured, with the results shown in Table 4. The volumes per formula unit are plotted versus the absolute temperature in Fig. 2. It is seen that, aside from the value of 623° K., all of the points lie on a smooth curve. The value at 623° K. is also the one most likely to be inaccurate. It seems quite reasonable

Table 4. Crystallographic data on $LaAlO_3$ at various temperatures

Temperature (°C.)	Primitive rhombohedral		Face-centered rhombohedral		Vol. per formula unit (\AA^3)
	a (\AA)	α	a (\AA)	α	
25	5.357	60° 6'	7.580	90° 5'	54.45
200	5.367	60 4	7.593	90 3	54.75
250	5.371	60 3	7.600	90 2	54.85
350*	3.803†	—	—	—	55.00
400*	3.806†	—	—	—	55.13
500	3.811†	—	—	—	55.35
650	3.818†	—	—	—	55.66

* See text.

† Cubic.

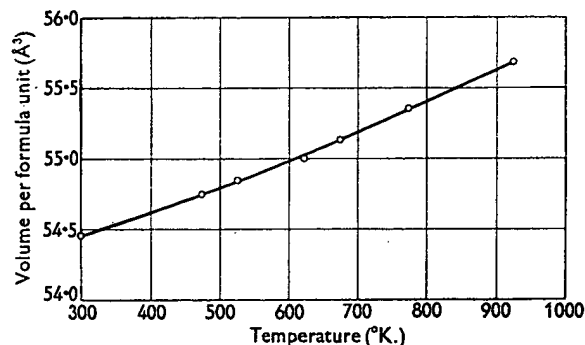


Fig. 2. A plot of volume per formula unit of $LaAlO_3$ versus absolute temperature.

to conclude that the transition from the rhombohedral to the cubic is of higher than first order.

A powder photograph was taken of $PrAlO_3$ at 950° C. At this temperature $PrAlO_3$ is still rhombohedral with the lattice constants $a_p = 5.364 \text{ \AA}$, $\alpha_p = 60^\circ 10'$. The face-centered rhombohedron has the dimensions $a_f = 7.586 \text{ \AA}$, $\alpha_f = 90^\circ 9'$. If the primitive rhombohedron is referred to a hexagonal cell, the hexagonal axes are $a = 5.378$, $c = 13.12 \text{ \AA}$.

In the case of the orthorhombic orthoferrites, no crystallographic transition was found below 845° C. Differential thermal analysis by P. D. Garn of one sample of $LaFeO_3$ indicated a transition at 980° C. (I). There appeared to be greater promise of a transition in the $SmAlO_3$ for two reasons: the intensities of reflections with odd l or odd $(h+k)$ appeared lower relative to those with $(h+k)$ even, l even (see Table I in this paper and in I), thus indicating less distortion from the ideal perovskite than in the $LaFeO_3$ case; the $SmAlO_3$ pseudocell has more nearly cubic dimensions than that of the $LaFeO_3$ (this is ascertained by comparison of the powder photographs of $SmAlO_3$ and $LaFeO_3$, rather than by the calculated lattice constants alone).

P. D. Garn carried out a differential thermal analysis of $SmAlO_3$ and found a large endothermic reaction at about 800° C. A similar analysis of $LaAlO_3$ did not locate a transition. This is an indication that the $SmAlO_3$ transition is probably first order. A powder

photograph of SmAlO_3 taken at 900°C . indicated a transition to the rhombohedral structure, but this is yet to be confirmed.

Discussion

With regard to crystallographic transitions in the rare earth aluminates, it is established that at least one of the rhombohedral compounds, LaAlO_3 , transforms to the cubic. There is indication that PrAlO_3 tends toward the cubic with increase in temperature and presumably this is true also of NdAlO_3 . The link between the orthorhombic structure and ideal perovskite is yet to be established conclusively, although it does appear that it goes through the rhombohedral.

In Tables 2 and 3 one sees that in the case of the orthorhombic structures the lattice constants behave quite similarly to those of the orthoferrites (see above concerning the SmAlO_3). As the A^{3+} ion gets larger the following relation is approached: $a = b = c/\sqrt{2}$, or in the pseudocell it seems that one might expect that $a (= c) = b$ and $\beta = 90^\circ$. Actually it appears that a rhombohedral pseudocell is obtained with increase of A^{3+} ion size and the cubic structure is not attained at room temperature in any of the compounds so far studied involving a pure trivalent rare earth as A^{3+} ion and a trivalent B ion. An a axis of the rhombohedral structure is in the first approximation comparable with the a or b axes of the orthorhombic structure. One may imagine that from the NdAlO_3 on, the ionic-size relationship is such that the a axis of a possible orthorhombic structure has caught up with the b , but that a substantial deviation from the cubic structure continues to exist. This indicates that there is a resistance in these compounds to the formation of the strictly regular octahedral bonding of oxygen ions to the Al^{3+} ion. It is evident, however, that in the rhombohedral compounds of this series the resistance to the formation of regular oxygen octahedra is overcome by increasing the thermal vibration amplitudes of the ions. The increase in vibration amplitude allows the ions to shift toward the positions of the ideal perovskite structure. Similar reasoning has been applied in a discussion of LiNbO_3 by Megaw (1954). A simultaneous effect from increase in temperature is increase in size of the ions; the apparent increase in size of the oxygen ions is particularly noticeable.

The oxygen ion is very accommodating as far as size is concerned; if one thinks of the ideal perovskite as a cubic close packing of oxygen and A^{3+} ions with the B^{3+} ions in octahedral holes there is quite a range in closest approach between oxygen ions. In cubic BaTiO_3 , for example, this distance is as high as 2.84 \AA , whereas in cubic LaAlO_3 it is as low as 2.69 \AA . A discussion of radii will be given in a subsequent paper, which will include the rare earth orthochromites, scandates, gallates and vanadites.

As described in I (see Table 4 of that paper) the minimum average interionic distances in these com-

pounds may be determined by assigning an ideal cell to the compound with cell edge equal to the cube root of the volume per formula unit. The distances for the aluminates are given in Table 5.

Table 5. Minimum average interionic distances in the aluminates

A^{3+} ion	$\text{A}^{3+}-\text{A}^{3+}$	$\text{A}^{3+}-\text{O}^{2-}$	$\text{Al}^{3+}-\text{O}^{2-}$
Gd	3.728 Å	2.636 Å	1.864 Å
Eu	3.732	2.639	1.866
Sm	3.738	2.644	1.869
Nd	3.749	2.651	1.875
Pr	3.762	2.660	1.881
La	3.790	2.680	1.895
Y	3.705	2.620	1.853

Table 5 is useful in that it indicates trend. Actually, the average $\text{Al}^{3+}-\text{O}^{2-}$ distances are probably each slightly longer than shown, but indicated differences of the magnitudes are to be expected from compound to compound. For example, the $\text{Ti}^{4+}-\text{O}^{2-}$ distances in cubic SrTiO_3 and BaTiO_3 are different, being a result of the different sizes of the Sr^{2+} and Ba^{2+} ions.

Several of the compounds discussed herein have been investigated previously by some other authors. (The paper by Keith and Roy (1954), a study which includes compounds discussed here and also in I and IV, will be discussed in IV.) Most recently Ruggiero & Ferro (1955) investigated the aluminates, orthoferrites and orthochromites of the rare earths. Their work was based solely on powder diffraction data, and perhaps for that reason does not give the end results described either herein or in I, nor to be given in subsequent papers in this series. For example, they report that although trigonal symmetry is not excluded, LaAlO_3 is monoclinic with a doubled cell which is close to cubic in dimension. For the sake of brevity, the reader is referred to the above paper for further information on the work of these authors.

The most recent work on YAlO_3 has been done in these Laboratories and described in I. Work of other investigators on that compound was discussed in that paper.

Naráy-Szabó (1947) has investigated LaAlO_3 and has called this compound monoclinic also, i.e. isomorphous with LaFeO_3 which he had probably indexed on a B -centered monoclinic cell (see I). This is probably the so-called doubled cell referred to by Ruggiero & Ferro. Naráy-Szabó gives 7.58 kX. (?) as his cell edge (the monoclinic cell supposedly has very nearly cubic dimensions). This is just the edge of the face-centered rhombohedral cell, as described above.

Because PbO is the solvent used for the oxides we have found a lead impurity in some of the aluminates. We have, however, felt that these are occlusions rather than a solution of the lead in the aluminate. To check this a LaAlO_3 sample was made by heating a mixture of the oxides at 1200°C . for 4 hr. A powder photograph of this sample indicated no difference in lattice

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constants. The YAlO_3 described in I was extremely pure; the largest impurity was $< 0.03\%$ Pb. Analyses were also made of the EuAlO_3 and NdAlO_3 . The former seemed to contain a substantial amount of lead ($> 1\%$) and the latter had a minor ($0.1\text{--}3.0\%$) Sm impurity. Although we feel that most of the lead was occluded, it is not impossible that very small amounts did dissolve in the EuAlO_3 (since we have no proof of the contrary) and it is very probable that all the Sm is dissolved in the NdAlO_3 . This, however, does not detract significantly from the results described herein, particularly since the trend of lattice-constant variation is the same as that shown in the orthoferrites and in the other series studied. Also, checks of the sort made for LaAlO_3 described above give confirmatory evidence that the Pb is not interfering significantly.

An interesting experiment related to this work was carried out on BaTiO_3 to see whether weak superstructure reflections have gone unnoticed in the past. As described above, the superstructure reflections of the rhombohedral aluminates are very few and very weak (e.g. see Table 1). It would not be impossible to overlook the two lines on the LaAlO_3 powder photograph, for example, or the few on the oscillation photographs used to align the PrAlO_3 crystal. It could also happen that none of the superstructure reflections would be strong enough to show on a powder photograph of normal exposure. For this reason, a BaTiO_3

crystal was photographed on a Buerger precession camera as follows: settings were made for the first layer assuming the repeat distance to be twice the known one; that is, settings were made for the '1/2th layer' with the tetragonal c axis as the precession axis. Mo K radiation filtered with Zr was used; exposure time was 72 hr. No reflections were observed.

The authors wish to thank J. P. Remeika for supplying the crystals for this investigation, E. A. Wood for the optical examinations, and P. W. Anderson and M. A. Gilleo for discussions relative to this work.

The spectroscopic analyses made by W. Hartmann, the IBM calculations of d spacings carried out by Miss D. P. Booth and the drawings made by H. S. Seubert are gratefully acknowledged.

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The Structure of Tetragonal Copper Ferrite

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(Received 7 May 1956 and in revised form 19 June 1956)

Copper ferrite, CuFe_2O_4 , is a tetragonally distorted inverse spinel. Since neutron diffraction measurements have shown no evidence for cation ordering on the octahedral sites, the structure parameters have been determined assuming the space group $D_{4h}^{19}\text{--}I4_1/amd$. The oxygen octahedra are elongated parallel to the c axis, but the FeO_4 tetrahedra are undistorted, and have the same dimensions found in cubic inverse ferrites. The magnetic structure is consistent with the Néel model of ferrimagnetism.

Introduction

Weil, Bertaut & Bochirol (1950) have shown that copper ferrite, CuFe_2O_4 , has a structure which is a distortion of the spinel structure. They found that if a sample was heated to a temperature above 760°C . and then rapidly quenched to room temperature, the structure was cubic, but was neither the normal spinel structure, with divalent ions in the tetrahedral

'A' sites and trivalent ions in the octahedral 'B' sites, nor the inverse spinel structure, with trivalent ions in the A sites, and the B sites occupied by divalent ions and trivalent ions at random. It was rather a disordered structure, with both kinds of ion in both kinds of site. By treatment at temperatures below 760°C . these authors produced samples whose crystal structure was tetragonal, with a c/a ratio, as referred to a face-centered cell, increasing with decreasing temperatures, and reaching 1.06 at 20°C . They also found that the increase in the c/a ratio was accom-

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